Spin frustration and metamagnetic behavior in a molecular-based quasi-1D ferrimagnetic chain: (MnTPP)(TCNE)

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We report an experimental observation of spin frustration and metamagnetic behavior in a quasi-1D ferrimagnetic chain, $(MnTPP)^{+}(TCNE)^{-}$. Metastability, hysteresis effects, and irreversibility of thermal and magnetic histories are observed in magnetization measurements. The "memory" phenomenon is seen in the temperature dependence of the thermoremanent and isothermal remanent magnetization. This system may be relevant to the magnetic behavior of the quantum/classical spin chains. The isothermal $M(H)$ at $T=2.25$ K supports a first order transition which may be related to effects of local anisotropy.

I. INTRODUCTION

The electron transfer compound $[MnTPP]^{+\cdot}[TCNE]^{-\cdot}$ (TPP=*meso*-tetraphenylporphin-ato, TCNE=tetracyanoethylene) has unusual magnetic properties and has recently been shown to exhibit hysteretic behavior up to ~5 K.[1] Single-crystal x-ray diffraction studies[1] reveal that the solid-state motif is a linear chain comprised of alternating donors and acceptors $\cdots D^{+}A^{-}D^{+}A^{-}\cdots$ along the chains (D=MnTPP; A=TCNE) where the $[TCNE]^{-\cdot}$ is *trans*-μ_2-σ-bound to Mn with a 2.305(4) Å separation and with a Mn-*N*-*C* angle of 148.1(4)°. The intrachain Mn···Mn separation is 10.116 Å, while the interchain in-registry Mn···Mn separations are 13.269 and 14.932 Å and the out-of-registry Mn···Mn separations are 11.006, 11.832, and 13.838 Å. Based upon $\nu_{C\equiv N}$ infrared data, the acceptor was ascribed to be $S=\frac{1}{2}$ $[TCNE]^{-\cdot}$ and the cation $S=2$ $[MnTPP]^{+\cdot}$.[1] The observed room-temperature effective moment, $\mu_{\text{eff}}[\equiv(8\chi T)^{1/2}]$, is $5.12\mu_B$ which is consistent with a value of $5.20\mu_B$ expected for $S=2$ and $\frac{1}{2}$ radicals, assuming an isotropic $g=2.00$.[1] An apparent minimum in χT vs T observed at ~310 K is indicative of ferrimagnetic behavior.[1–3] Because of large interchain separation and no chemical bonding between the chains, this system may well represent a one-dimensional (1D) magnetic chain. In addition, this system is unique in the presence of alternating $S_A=\frac{1}{2}$ and $S_D=2$ enabling tests of theories concerning alternating quantum/classical spins.

Recently there has been increased theoretical interest in 1D magnetic chain systems. Among current problems are: (1) magnetic behavior of mixed quantum/classical spin systems;[4] (2) effects of local anisotropy on metamagnetic Ising chains;[4,5] (3) the possibility of a Haldane gap in mixed integral and half-integral spin systems; and (4) the effect of random magnetic anisotropy (RMA) in an XY ferromagnetic chain.[6,7] Although theoretical studies of the spin nature and ground state of 1D systems have made remarkable progress, many aspects predicted by recent theories have not been verified yet by experiments. For example, for the Ising model, exact expressions of the susceptibility calculated from a general quasiclassical treatment show that the sublattice magnetizations can nearly or exactly compensate each other.[4] Also, by introducing a single-ion anisotropy within a ferrimagnetic Ising chain, a transfer matrix calculation[5] showed that with strong local anisotropy the sublattice magnetization of classical spins can be stabilized perpendicular to the applied field; hence the usual metamagnetic behavior may not occur. As another example, recent Monte Carlo simulations show that an XY ferromagnetic chain with a weak RMA has significant hysteresis.[6,7] These nonequilibrium effects depend strongly upon the initial conditions. Thus, one may expect nonergodic or glassy behavior due to memory effects even within laboratory time scales at low temperature. Experimentally, therefore, it is of interest to study the magnetic properties of an anisotropic ferrimagnetic chain.

II. EXPERIMENT

The magnetization was measured using a Faraday balance magnetometer in the temperature range of 2.1–300 K with applied magnetic field up to ~80 kG. The field gradient is separately controlled and is typically ±20 G/cm. The isothermal data were taken under a field sweep speed <0.7 kG/min below 4.2 K and <0.2 kG/min above 4.2 K. The cooling and heating rates in the temperature-dependent measurements were less than 0.5 K/min. The temperature dependence of thermoremanent magnetization (TRM) was measured by setting zero field (earth field plus a small remanent field in the superconducting magnet) after field cooling (FC) from $T>30$ K to ~2.2 K. The isothermal remanent magnetization (IRM) data were obtained by cycling the applied field $0\rightarrow H\rightarrow 0$ at ~2.1 K after a zero-field cooling (ZFC). The saturation moment M_s at low temperature was found to vary among different preparations of the samples. $M(T,H)$ at 2.25 K and 80 kG was found to be around 2.2×10^4 emu G/mol for a packed powder sample and 2.9×10^4 emu G/mol for a loose polycrystalline sample,[1] though the high-temperature susceptibility is the same for both. This could be caused by the effects of crystal anisotropy. The data presented in this article are normalized as M/M_s.

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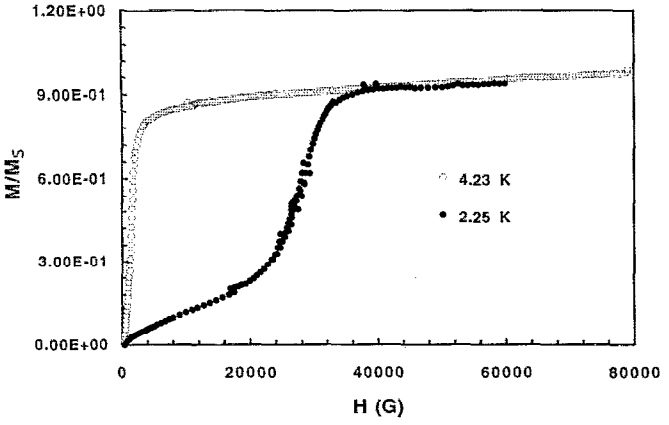

FIG. 1. Isothermal magnetization vs field after zero-field cooling (increasing fields).

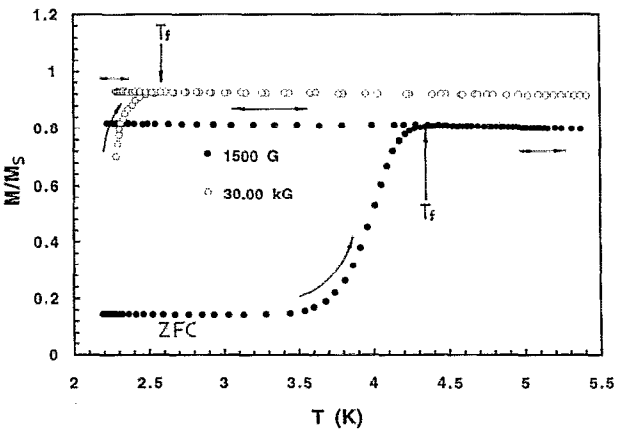

FIG. 2. Isofield magnetization vs temperature.

III. RESULTS AND DISCUSSION

Strong magnetic hysteresis behavior is observed for temperatures up to ~ 5 K. The hysteresis is dependent on the field sweep rate, which implies that the system's spin configuration consists of metastable states. Figure 1 shows the results of ZFC magnetization versus field at 4.23 and 2.25 K with increasing field. At 2.25 K the magnetization increases rapidly above ~ 20 kG. If one assumes a usual 3D ordering at 2.25 K, then the inflection point (~ 30 kG) where the slope of M vs H exhibits a "near" divergence may be recognized as the critical field corresponding to a spin-flip transition. In principle, the magnetization should be discontinuous at a first-order transition. The continuous S-shape portion of magnetization observed in our case might be caused by the (1) demagnetizing effect; (2) fast field sweep; and/or (3) use of powdered sample. In general, even for a single-crystal sample under a sufficiently slow field sweep speed (so that equilibrium state can be reached), a small misalignment between an applied field and the easy axis will cause a first-order transition to smear.[8] The S-shaped portion in the M vs H curve changes dramatically between 2.25 and 4.23 K (Fig. 1). If there is indeed 3D ordering (due to a weak interchain interaction), it is suggestive that it only dominates below ~ 4 K. The rapid increase of isothermal magnetization at low field at 4.23 K is reminiscent of zero-temperature predictions of a $(1+1)$-dimensional O(3) nonlinear σ model (with identical high spin)[9] and an exact numerical calculation[10] for an antiferromagnetic Heisenberg chain. For an integral spin chain, it is known that there is an energy gap and therefore there is no magnetization up to a finite threshold field.[11] Therefore, if the isothermal data at 4.23 K reflect 1D behavior, this spin alternating chain has mainly half-integral spin character.

The above discussion focuses on isothermal magnetization data. We now address the results of our isofield measurements. Figure 2 shows results of isofield magnetization versus temperature under the applied fields of 1.5 and 30 kG. With ZFC and FC, irreversible behavior is clearly seen below T_f indicated in Fig. 2. This behavior is a universal of spin frustration.[12] Here T_f is denoted as a freezing temperature at which a "spin-glass" transition occurs. With decreasing H, T_f increases. The highest T_f measured is ~ 6 K using $H \sim 100$ G. The substantial difference between FC and ZFC magnetization reflects a memory effect, which likely originates in a frustration. Also, we notice that the ZFC magnetization increases much more rapidly than for a usual spin-glass system. We should point out that, unlike the metallocenium salts,[13,14] TCNE lies essentially perpendicular to the plane of MnTPP and directly coordinates to the Mn.[1] One possible origin of frustration comes from a weakly antiferromagnetic superexchange J' between the Mn within the chain which may dominates below 4 K. Under a ZFC procedure the initial "antiferromagnetic" state can be frozen at a low temperature. As temperature increases, thermal fluctuations will destroy the initial state and the system then rapidly envolves through metastable states. A stabilized ordered state is eventually reached due to a compromise among the thermal fluctuations, spin frustration, and external field.

This metastability even extends to the high-temperature regime. Figure 3 shows the results of sponta-

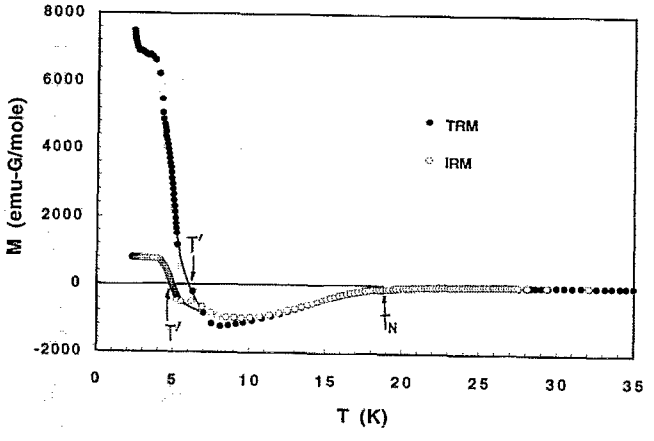

FIG. 3. Thermoremanent magnetization (TRM) and isothermal remanent magnetization (IRM) vs temperature (increasing temperature).

neous magnetization versus temperature. The TRM data were taken by a FC at 11.5 kG from $T > T_f$ to $T < T_f$ followed by setting $H=0$. The IRM was measured by cycling an external field $0 \rightarrow H(11.5\ \text{kG}) \rightarrow 0$ at ~ 2.1 K after a ZFC. The large difference of the moment between the TRM and IRM observed clearly indicates a memory effect.

Figure 3 also suggests the presence of a possible compensation phenomenon. The Néel ordering temperature is estimated to be 18 K and the compensation point T' as indicated in Fig. 3 is found to be different for the TRM and IRM, suggesting that the sublattice magnetizations within the two different spontaneous spin configurations compensate each other differently under thermal activation. The origin of compensation phenomena in a 1D chain is of interest. The classical behavior of the $S=2$ spin with the presence of local anisotropy has been predicted to lead to compensation phenomena even in the 1D case.[4] For the system studied here, the single-ion anisotropy of MnTPP is likely of order 2.0–3.0 cm^{-1} (~ 5 K).[15] With such an amount of local anisotropy, short-range ferrimagnetic order could possibly occur at a finite temperature[5] and the magnetic moment of $(\text{MnTPP})^+$ could rotate continuously toward the direction of an applied field and compensate the sublattice magnetization of $S=\frac{1}{2}$ for TCNE^-.[4,5] However, because the accuracy of the zero-field measurements is affected by the gradient field and the position and size of the sample, the measured compensation effect could be partially induced by relaxation in the magnetization and flipping of domains due to the presence of a small negative field. For further confirmation, an aging experiment with better zero-field control is in progress.

In summary, frustration and metamagnetic behavior have been observed in a quasi-1D chain. Due to the continuous character (high spin, $S=2$ for MnTPP), the magnetic moments carried by the classical spins align less efficiently than quantum ones ($S=\frac{1}{2}$ for TCNE). However, the frustration characterized by metastability, with hysteresis effects, and irreversibility of thermal or magnetic histories, is not well understood in the 1D case so far. This work provides experimental evidence of frustrated behavior of a 1D chain. Theoretical realization of frustration usually involves certain randomness. Recently theoretical studies on the XY chain with weak RMA have shown some features of distinct metastability and hysteresis effects.[6,7]

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